

Reply to comment on “Electronic structure and structural stability study of Li_3AlH_6 ”

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Abstract

The nature of the bonding in Li_3AlH_6 has been re-examined with additional analyses using density-functional calculations. From partial density of states, charge density distribution, charge transfer, electron localization function, crystal orbital Hamilton population and Mulliken population analyses it is concluded that the interaction between Li and AlH_6 in Li_3AlH_6 is ionic as earlier advocated. Based on charge density distribution, electron localization function, and density of states analyses we earlier suggested that the interaction between Al and H is largely of the covalent type. However, additional analyses indicate that the interaction between Al and H in the AlH_6 structural sub-units is of a mixed covalent ionic character (iono-covalent).

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The chemical bonding in materials becomes complicated to evaluate when the number of constituents increases. For binary compounds one can easily estimate the degree of ionic character from their electronegativities using Gordy's [1] approximation. For ternary and quaternary systems it is harder to estimate the bonding character. When we consider hydrides, it is even more complicated than for other compounds, because of the small size of the hydrogen and its only one valence electron which give rise to different bonding character for the hydrogen in different chemical environments (valence state +1 or -1 as well as covalent and metallic character). We have recently demonstrated these features in a series of metal hydrides.[2, 3] In our previous work [4] on Li_3AlH_6 , the main focus was on the structural phase stability and electronic structure but we also characterized the chemical bonding between the constituents based on results obtained from partial density of states (PDOS), charge density and electron localization function analyses. From these considerations we concluded without ambiguity that the interaction between Li and the AlH_6 structural subunit is ionic. Energetic degeneration of Al- p and H- s states (from DOS study), finite charge density distribution between Al and H, and the polarization nature of ELF at the H site toward Al, and the spatially constellation of Al and H led us to conclude that the covalent bonding prevails between Al and H in the AlH_6 subunit. Moreover, the electronegativity difference between Al and H is only 0.7, which also should favor covalent-type interaction between them.

A recent paper by Singh [5] on Li_3AlH_6 describes the bonding between H and Al as purely ionic. The arguments for this interpretation is based on DOS analysis and long-range Coulomb interactions according to calculations using the linearized augmented plane wave method. As more H- s states are present in the valence band (VB) than in the conduction band (CB), Singh concluded that the interaction between Al and H must be ionic. Aguayo and Singh [6] have also performed a similar type of analysis on NaAlH_4 where a similar conclusion was reached (viz ionic interaction between H and Al) The calculated DOS for Li_3AlH_6 by Singh is in perfect agreement with our findings.[4] Hence, there is no ambiguity between the different computational methods, whereas the interpretation/understanding of the results differs. It is commonly recognized that it is difficult to characterize the nature of chemical bonding (in particular for hydrides) from DOS and integrated charges inside spheres alone. We have recently shown that on using a combination of charge density, charge transfer and ELF distribution along with other information one should be able to characterize the

quite complicated chemical bonding in hydrides.[2] Hence in order to make a firm conclusion about nature of the chemical bond in Li_3AlH_6 we need more data from different perspectives. Hence, we have made additional calculations using advanced density-functional tools.

Each and every theoretical tool has some additional flexibility/facility to evaluate bonding behavior. Hence we have now used different density-functional tools to gather as much information as possible regarding the chemical bonding in Li_3AlH_6 . The calculations are made for the theoretical equilibrium structure parameters specified in Ref. 4 for Li_3AlH_6 , and for the compounds chosen for test cases we have used experimental structural parameters. The DOS, charge density, charge transfer, electron localization functions are evaluated from Vienna *ab initio* simulation package,[7] the crystal orbital population is evaluated using the TBLMTO-47 package.[8] The Mulliken population analyses have been made with the help of CRYSTAL03 [9] code in which we used 5-11G, 6-11G, 5-11G, 8-61G, and 85-11G basis sets for H, Li, Be, Mg, and Al, respectively.

The calculated partial DOS of Al and H in Li_3AlH_6 are shown in Fig. 1, illustrating the following three main features: (1) The VB and CB are separated by a band gap of ~ 3.8 eV confirming that this compound is an insulator. (2) The VB is split into two separate region by a ~ 1.3 eV energy gap. The lowest lying bands (at -7.5 to -5.8 eV) are mainly originated from Al *s* with finite contributions from H-*s* states. The second region from ~ -4.5 to -2.2 eV comprises energetically degenerate H-*s* and Al *p* states which we focused on as a favorable situation for formation of a covalent bonding in Ref. 4. The spherically symmetric nature of *s* orbitals together with the energetic degeneration of H-*s* and Al-*s* states, there should be a high probability for formation of covalent-type bonding between these atoms. (3) The very small contribution of H in the unoccupied states above the Fermi level (E_F) is explained with the help of COHP analysis. The COHP, which is the Hamiltonian population weighted DOS, is identical to the crystal orbital overlap population. Negative value of COHP indicates bonding character and the positive value of COHP shows anti-bonding character. The DOS and COHP are evaluated using different computer codes and that is the reason for the slight energy shift between the DOS and COHP curves in Fig.1, but the overall features are the same. The lower panel in Fig. 1 (lower panel) shows that bonding states are present below -6.5 eV and anti-bonding states between ~ -2.8 eV and E_F . This explains why there are few H-*s* states present in the CB.

If the chemical bonding between Al and H is purely ionic one would expect that Al-*p* and

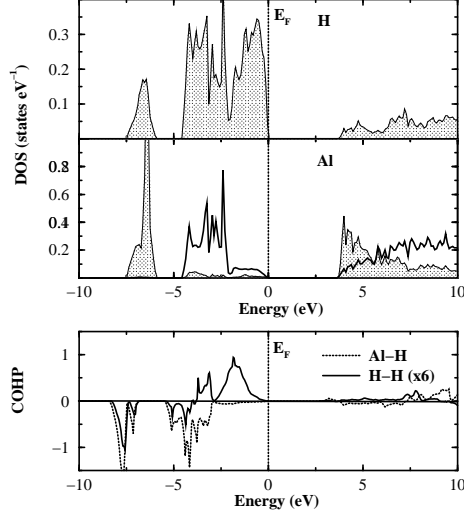


FIG. 1: Upper panels: Calculated site- and orbital-projected density of states for Al and H in Li_3AlH_6 ; s electron contributions are shaded by grey color. Lower panel: COHP for Al–H and H–H in Li_3AlH_6 .

H- s states should be energetically well separated.[10] Further, in a purely ionic situation one does not expect a finite electron density distribution between Al and H as Fig. 2a shows. Moreover the charge-density distribution should be spherically symmetric around the H site if the bonding is purely ionic. Hence we came to our initial conclusion that the bonding between Al and H in Li_3AlH_6 is largely covalent. For strong covalent bonding Singh [5] points out that the H character should be distributed between the three s - p manifolds. As the H- s character is very small in the CB (Fig. 1 upper panel), Singh concluded that covalent contribution is negligible. However, in the first place one can not judge the character of chemical bonding in complex materials based on DOS analyses alone (e.g. see Ref. 2). Owing to the ionic-covalent interactions all H- s orbitals will be filled and hence both bonding and antibonding states of the s - p hybrid are within the VB as evident from our COHP analysis (e.g., see Fig. 1 lower panel).

If the bonding interaction between all constituents in Li_3AlH_6 is purely ionic one would expect narrow band features and certainly not the broad DOS features found for Li_3AlH_6 which indicate overlap interaction between the constituents, viz. also for the purely ionic case the distinct DOS manifold around -7 eV with 2 electrons per formula unit are contributed by only one of the constituents. However, considerable amount of electrons (according to the integrated DOS which shows that this contribution is 36% from Al, 49% from H and

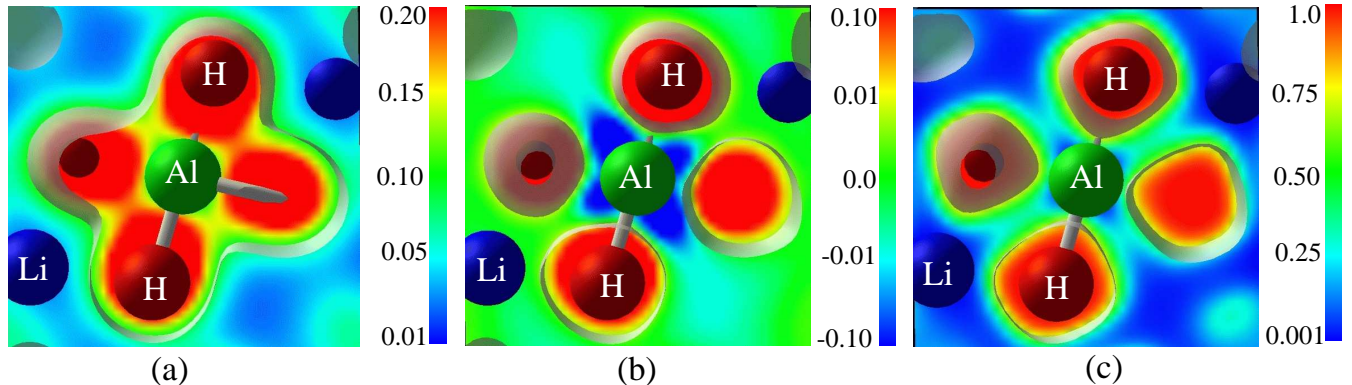


FIG. 2: (Color online) Calculated (a) valence-electron charge density, (b) charge transfer, and (c) ELF plot for α - Li_3AlH_6 .

the remaining 15% from Li) from both Al-*s* and H-*s* indicate a finite degree of covalent character. If Al is in the 3+ state, negligible amounts of electrons would be left at the Al site resulting in very small contribution from it to the VB. In fact, the integrated DOS yielded ~ 0.78 electrons at the Al site and shows that the bonding interaction is not purely ionic. The insulating behavior can be explained as follows: Within one Li_3AlH_6 unit, the 3 electrons from Li will fill 3 of the 6 half-filled H-*s* orbitals and the remaining 3 half-filled H-*s* orbitals form covalent interaction with the three electrons from Al resulting completely filled VB which gives the material insulating behavior.

In order to understand the chemical bonding in Li_3AlH_6 in detail Singh [5] performed a test calculation with the position of one Li in the unit cell exchanged with a H. Such an analysis is questionable because although Li and H have one *s* electron in the outermost shell the former always takes the 1+ valence state whereas the latter in the ionic case takes either 1+ or 1− depending on the chemical environment.

In order to gain further understanding of the nature of the bonding we have calculated the charge density, charge transfer, and electron localization function (ELF) for α - Li_3AlH_6 . The results are shown in Fig. 2, where we show only the relation between Al and H since there is no ambiguity with regard to the ionic interaction between Li^+ and AlH_6^- . The charge-density distribution and charge-transfer plot indicate that a finite number of electrons are present between Al and H, which means that there is a finite covalent type of interaction between Al and H within the AlH_6 unit. The charge transfer plot clearly indicates that charges are depleted from Al (Fig. 2b) and Li. The depletion is not spherically symmetric

at the Al site, which implies that the bonding is ionic with an appreciable covalent-type interaction (directional bonding) between Al and H. ELF is another useful tool to distinguish between different bonding situations in solids[11, 12]. The value of ELF is limited to the range 0 to 1. A high value of ELF corresponds to a low Pauli kinetic energy, as can be found for covalent bonds or lone electron pairs. The calculated ELF for Li_3AlH_6 is shown in Fig. 2c in which the H electrons are polarized toward the Al site. A similar character of the ELF is found for the molecules C_2H_6 and C_2H_4 , where the interaction between the C and H is commonly recognized as covalent.[12] Hence, one must conclude that there is a directional bonding character between Al and H in Li_3AlH_6 .

In order to make a quantitative conclusion it would be useful to be able to identify the amount of electrons on a particular atom and populations between atoms. Although there is no unique definition of how many electrons that are associated with an atom in a molecule or a sub-unit of a solid it has nevertheless proven useful in many cases to perform population analysis. Due to its simplicity the Mulliken [13] population scheme has become the most familiar approach to count the electrons associated with a given atom. However also this method is more qualitative than quantitative, giving results that are sensitive to the atomic basis. Mulliken charges are reported in Table 1 for series of H-based test materials using examples which may provide benchmarks for systems with well recognized chemical bonding. LiH is a purely ionic compound and the calculated Mulliken charges reflect nearly pure ionic picture with Li^+ and H^- . Also, the overlap population between Li^+ and H^- is close to zero, as expected for an ionic compound. Similarly in MgH_2 , BeH_2 , and AlH_3 the bonding interaction is mainly ionic but the degree of ionicity is reduced from MgH_2 to BeH_2 and further to AlH_3 viz these compounds exhibit some covalent character as evidenced by the non zero overlap population. For the CH_4 molecule the overlap population takes a value of 0.384 consistent with the well known covalent interaction for this molecule. The Mulliken effective charges for Li, Al and H in LiAlH_4 and Li_3AlH_6 indicate that the interaction between the Li and $\text{AlH}_4/\text{AlH}_6$ is ionic (one electron transferred from Li to $\text{AlH}_4/\text{AlH}_6$). There is a finite overlap population between Al and H within the $\text{AlH}_4/\text{AlH}_6$ units which reflects a partly covalent character of the Al–H bond. However, the magnitude of overlap population is smaller than for purely covalent compounds. Also, the partial charges (around two electrons transferred from Al to H) implies that significant ionic contribution to the Al–H bond. The calculated ICOHP indicates that the covalent Al–H interaction in LiAlH_4

TABLE I: Mulliken population analysis for selected hydrogen containing compounds. The Mulliken effective charges (MEC) are given in terms of e .

| Compound | Atom | MEC | Overlap population |
|----------------------------------|------|-------|--------------------|
| LiH | Li | +0.98 | −0.003 (Li–H) |
| | H | −0.98 | |
| CH ₄ | C | −0.26 | 0.384 (C–H) |
| | H | +0.06 | |
| MgH ₂ | Mg | +1.87 | −0.040 (Mg–H) |
| | H | −0.93 | |
| BeH ₂ | Be | +1.63 | 0.045 (Be–H) |
| | H | −0.82 | |
| AlH ₃ | Al | +2.22 | 0.091 (Al–H) |
| | H | −0.74 | |
| LiAlH ₄ | Li | +1.01 | 0.171 (Al–H) |
| | Al | +2.01 | −0.021 (Li–H) |
| | H | −0.75 | |
| Li ₃ AlH ₆ | Li | +1.01 | 0.105 (Al–H) |
| | Al | +2.08 | −0.020 (Li–H) |
| | H | −0.85 | |

is stronger than that in Li₃AlH₆. Similarly, the calculated Mulliken effective charges and overlap population indicates that the covalent Al–H interaction is reduced when we move from LiAlH₄ to Li₃AlH₆.

As a conclusion we thus find that the bonding nature of the hydrides LiAlH₄ and Li₃AlH₆ do not exhibit simple ionic or covalent character. In fact the bonding interaction in these compounds is quite complicated. The interaction between Li and AlH₄/AlH₆ is ionic and that between Al and H comprises of ionic and covalent character. We believe that similar type of bonding situation prevails in all similar hydrides, but the magnitude of the ionic/covalent mixture will exhibit considerable individual variation. Our study indicates that several analyses must be performed in order to make a finite conclusion regarding the bonding nature of such materials.

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